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TECHNICAL REPORT #70

"Spectroscopic Observation of Individual sp^3-Nitrogen Stereoisomers. Supersonic Jet Studies of 2-Aminobenzyl Alcohol"

by

Jeffrey I. Seeman, Henry V. Secor, Hoong-Sun Im, and E. R. Bernstein

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Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

May 13, 1990

Spectroscopic Observation of Individual sp^3-Nitrogen Stereoisomers.

Supersonic Jet Studies of 2-Aminobenzyl Alcohol

Jeffrey I. Seeman* and Henry V. Secor

Philip Morris Research Center

P.O. Box 26583

Richmond, Virginia 23261

Hoong-Sun Im, and E. R. Bernstein*

Department of Chemistry

Condensed Matter Sciences Laboratory

Colorado State University

Fort Collins, Colorado 80523

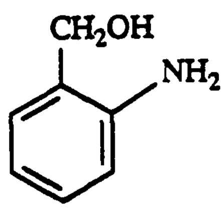
Conformational analysis of the trivalent nitrogen atom is conceptually complicated because of the presence of two dynamic processes, nitrogen inversion and internal rotation about various single bonds.[1-7] Experimental investigations of this subject are further entangled because these conformational interconversions have very low barriers and are rapid on the time scale of most experimental observations.[8] Evaluation of the stereodynamics of these systems has typically required one of three "tricks" to slow the inversion and/or rotation rates:[1-7] (a) use of electronegative substituents, e.g., N-Cl derivatives; (b) examination of sterically crowded substrates; or (c) presence of acid or hydrogen bonding solvents. We herein report the first observation of spectra of individual isotopomers of a monosubstituted amine RNH^1H^2 in which H^1 and H^2 represent diastereotopic hydrogen atoms under slow exchange conditions.

Nitrogen-Chlorine

Keywords; ORGANIC Compounds, Spectroscopy, Amines, Benzyl Radicals, Alcohols, Isomers (JG)

Minimum energy conformation(s) of a variety of alkyl- and hetero-substituted aromatic compounds have been observed and their conformations determined by supersonic molecular jet laser spectroscopy.[12-20] Laser jet spectroscopy has a number of particular advantages for conformational analysis: the expansion results in molecules at near 0 K, thereby slowing the rates of conformational interconversions and/or chemical exchange; one 0_0^0 (origin) transition is observed for each individual stable conformation; the molecules are isolated; and the resolution of experiment is excellent (ca. 0.4 cm^{-1}).

The mass resolved excitation spectrum (also sometimes refered to as the time of flight mass spectrum, TOFMS)[21] of 2-aminobenzyl alcohol (1) is shown in Figure 1a. In addition to a 0_0^0 transition at 33 308.0 cm^{-1}, five other intense transitions are observed within the first 300 cm^{-1} of the spectrum. The spectrum of 1 is similar to that observed for benzyl alcohol (2), which was shown by laser jet spectroscopy to have a single stable ground state conformation in which $\tau(C_{ortho}-C_{ipso}-C_{\alpha}-O) = 90°$, i.e., a perpendicular conformation.[12]



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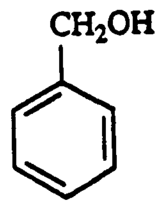

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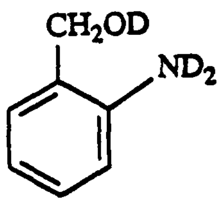
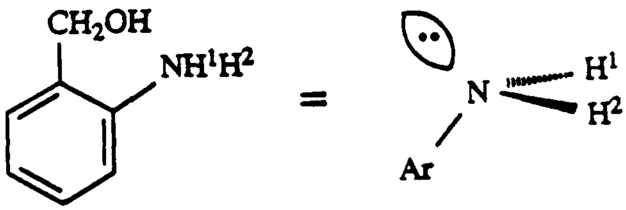
It is extremely unlikely that all six transitions shown in Figure 1a are origin transitions. When compared to its all protiated parent, a deuteriated analogue's first 0_0^0 transition will typically shift to the blue (to higher energy) while all vibronic transitions will shift to the red (to

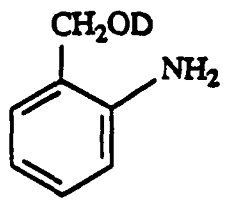
lower energy) relative to that origin. These isotope effects allow one to distingish between origin and vibronic transitions. To establish the number of 0_0^0 transitions, 2-aminobenzyl alcohol-d_3 (3) was prepared and examined. The mass resolved excitation spectrum of 3 is shown in Figure 1d. A comparison of Figures 1a and 1d demonstrates that only a single origin transition is present in each spectrum. In addition, the isotope shifts demonstrate that the observed progressions are due to motion of the entire CH_2OH group in the excited electronic state.

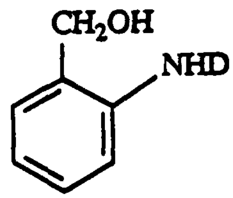


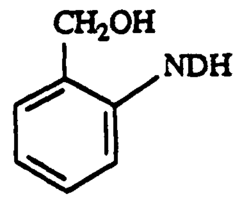


3 4

We now consider distinguishing between 2-aminobenzyl alcohol species in which the amino hydrogen atoms H^1 and H^2 are nonequivalent, as symbolized by 4.[8] The $S_1 \leftarrow S_0$ spectrum observed in mass channel <u>m/z</u> 124 [corresponding to 2-aminobenzyl alcohol-d_1 (5)] is shown in Figure 1b. The spectrum of 5 is readily interpretable based on the spectra of 1 and 3: each single transition of 1 and 3 has become a triplet in the spectrum of 5. The triplet can be further resolved into a single feature to low energy (ca. 10 cm^{-1}) and a doublet (resolved by ca. 1 cm^{-1}). We interpret these three peaks as arising from three monodeuteriated isotopomers of 1, 5a-5c. The



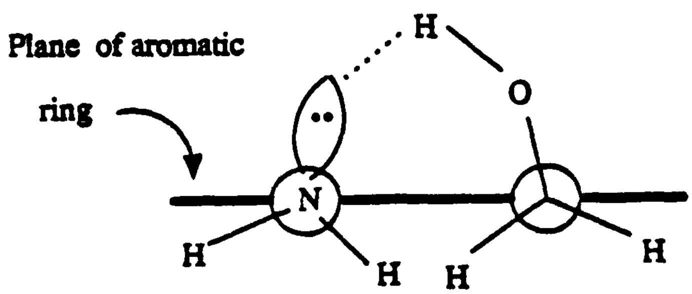




5a 5b 5c

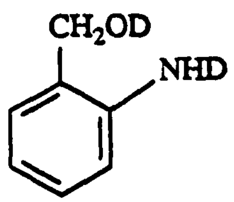
lowest energy feature of the triplet is suggested to arise from 5a, while the doublet feature is suggested to be associated with structures 5b and 5c, in which the two amino hydrogen atoms are diastereotopic. Figure 1b consequently is a superposition of three spectra, one each for 5a-5c. Based on the perpendicular conformation of benzyl alcohol,[12] and on the expected intramolecular hydrogen bonding in 1 in the expansion gas (c.f. below), Scheme I illustrates our proposed approximate geometry for 2-aminobenzyl alcohol.

Scheme I.

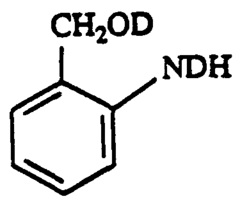


This assignment is confirmed by the mass resolved excitation spectrum observed when monitoring mass channel m/z 125 for 2-aminobenzyl alcohol-d_2 (6) shown in Figures 1c. This spectrum is remarkably similar to the

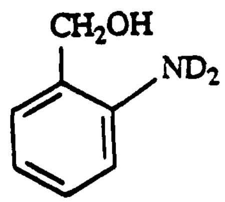
spectrum of 5 (Figure 1b) with the exception that the relative positions of the singlet and the doublet are interchanged. Based on the above considerations, Figure 1c arises from the superposition of features from the spectra of 6a-6c.



6a



6b

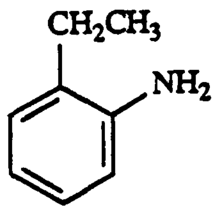


6c

The individual diastereomers of 5 and 6 are thus each stable over the time scale of the experiment and can be observed uniquely. The spectra of 5a-5c and 6a-6c are consistent with the number of isomers for each compound and the observation that deuterium substitution on the nitrogen atom produces a larger $S_1 \leftarrow S_0$ isotope shift than deuterium substitution on the oxygen atom. The switch in singlet-doublet positions going from Figure 1b to Figure 1c is also consistent with the location of the deuterium atoms in 5a-5c compared to 6a-6c: the lowest 0_0^0 transitions obtain for the species having a CH_2OD moiety. Upon optical excitation ($S_1 \leftarrow S_0$), the force constants for the amino moiety must change more than those of the hydroxyl moiety. The barrier to inversion/rotation at the amino nitrogen atom of 1 is thus substantial and considerably larger than the zero point energy in this coordinate.

To examine the nature of the amino group inversion/rotation barriers and role of hydrogen bonding in the system, the spectra of 2-ethylaniline

(7) and its mono- deuteriated analogues are examined. A single 0_0^0 transition is observed for each of these two compounds, suggesting that the inversion/rotation barriers about the amino group nitrogen atom of 7 is small, less than the zero point energy in those coordinates. Similar conclusions have been reached for the essentially free rotation for the methyl group of 1-ethyl-2-methylbenzene (8),[13,14] a substrate isosteric with 7. Thus the barrier to inversion/rotation at the amino group must be relatively small (of the order of the zero point energy) for 7. The barrier to inversion/rotation at the amino group of 1 must have a substantial contribution from hydrogen bonding between the amino group lone pair electrons and the hydrxyl hydrogen atom.



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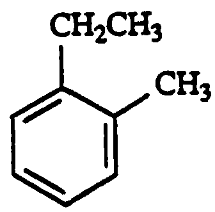

8

To our knowledge, this work represents the first experimental observation of spectra of the individual isotopomers of a monosubstituted amine. Further, all previous studies of diastereotopic non-quaternary amines have generally involved tertiary nitrogen either in a small ring system or with at least one heteroatom directly bonded to the nitrogen.

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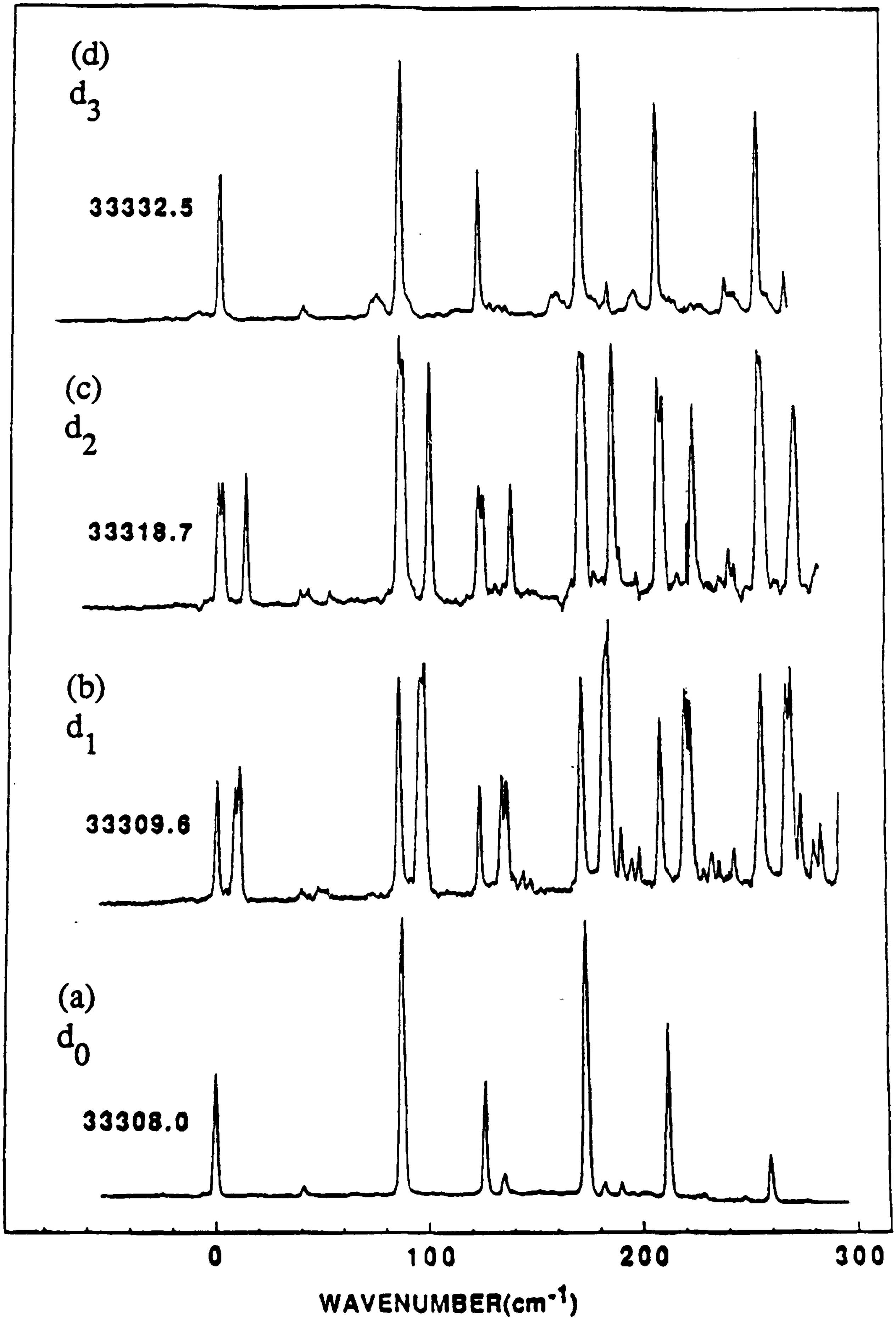
(21) The experiment is performed as follows. A sample is irradiated with a laser of energy ν_1, resulting in the generation of the first excited singlet state ($S_0 \rightarrow S_1$). A second photon ν_2 subsequently ionizes those molecules in S_1 ($S_1 \rightarrow I^+$). The ions are detected in given mass channels by time of flight mass spectroscopy, such that only ion current representing a chosen m/z is recorded. The energy of the ν_1 laser is changed, and an absorption spectrum of a mass selected species is obtained.

(22) Under conditions in with rotation about $\tau(C_2$-C_1-C_α-O) is frozen, H^1 and H^2 are diastereotopic.

Figure 1. Mass resolved excitation spectra of 2-aminobenzyl alcohols.



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